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Theoretical and experimental study of diffuse reflectance spectra of semitransparent particulate matter

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Abstract : An expression correlating diffuse reflectance of semitransparent particulate matter with optical and morphological properties of particles has been derived. The validity of proposed expression has been studied by comparing theoretically calculated and experimentally measured reflectance spectra of powdered samples. Overall evaluation of the proposed theoretical expression is made by calculating CIELAB colour difference parameter between measured and calculated diffuse reflectance spectra.

Keywords : Diffuse reflectance spectra, reflectance by semitransparent particulate matter, particle model theory

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1. Introduction

Theoretical aids for diffuse reflectance spectroscopy for particulate matter are used either to determine optical and/or morphological properties of particles or to predict reflectance spectra of powdered samples [1–5]. Mathematical descriptions of reflectance spectroscopy are based mainly on two physical models *e.g.* treating the sample as continuous media or as ensemble of particles. Continuous media theories use the differential equation method to derive the theoretical expression for diffuse reflectance. In this group, the theory proposed by Kubelka and Munk is by far the most widely used theory [6,7]. The main drawback in this theory is that the diffuse reflectance is described in terms of arbitrary constants rather than fundamental optical parameters of the particles Theoretical formulations based on second physical model, are known as particle model theories [8–12]. In this approach, the statistical summation over discrete particles reflecting/refracting light diffusely according to laws of geometrical optics are used to correlate diffuse reflectance with optical and morphological properties of particles. The striking features of particle model theories are that the diffuse reflectance of particulate samples is related to size and refractive index of particles. Comparative study of different particle model theories has been made by various authors [13,14]. In the present form, particle model theories can be applied to samples at infinite thickness *i.e.* the substrate on which the particulate sample is resting do not contribute to reflectance. On the other hand, Kubelka-Munk theory can be applied to semitransparent or transluscent media. In practice, it is often required to obtain information about size and/or nature of particles from semitransparent samples of atmospheric dust, samples collected during dust storms, pollutant collected through air samples or many chemical crystalline layers. In this paper we have made an attempt to derive expression for semitransparent particulate layer, correlating reflectance with size and refractive index of the sample.

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2. Theoretical formulation

To derive the expression for diffuse reflectance of semitransparent particulate media, we consider a particulate system of finite thickness and resting on a substrate of reflectance R_g as shown in Figure 1. The sample is assumed to be divided into layers of size equal to average particle size in the sample. The surface of the sample is illuminated with monochromatic light of intensity I_0. The attenuation of radiant energy while propogating through a layer is assumed to be 'A' fraction of energy in the beam. Therefore, the intensity I_1 of downward going beam emerging through the first layer is given by

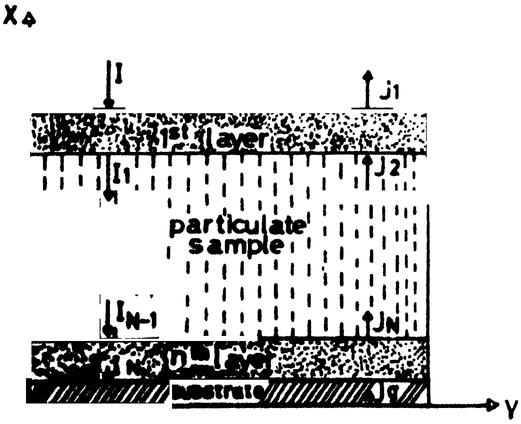

Figure 1. Physical model adopted to derive proposed theoretical equation.

$$I_1 = I_0(1-A). \tag{1}$$

Here, the parameter A is called absorption coefficient and is assumed to be related to fundamental optical and morphological characteristics of particles as proposed by Simmons [5] by the relation

$$A = (2/3)n^2kd, \tag{2}$$

n is real part of refractive index. k is often called as absorption index and is related to imaginary part of refractive index by relation $n_{IM} = k\lambda/4\pi$. d is diameter of particle expressed in cm. Similarly the radiations I_2 emerging through second layer is given by

$$I_2 = I_1(1-A)$$

or,

$$I_2 = I_0(1-A)^2. \tag{3}$$

Adopting this nomenclature, the radiations transmitted through N-th layer and incident on the substrate is given by relation

$$I_N = I_0(1-A)^N. \tag{4}$$

Light reflected from substrate of reflectivity R_g and moving in upward direction is given by

$$J_g = I_N R_g. \tag{5}$$

Intensity of radiation of J_N emerging from N-th layer in upward direction is given by

$$J_N = J_g(1-A). \tag{6}$$

Finally, light coming out from first layer is given by

$$J_1 = J_g(1-A)^N. \tag{7}$$

Reflectance of semitransparent particulate sample is given by relation

$$R = J_1/I_0. \tag{8}$$

Using eqs. (4), (5) and (7), reflectance of particulate sample resting on a substrate of reflectivity R_g is given by

$$R = R_g(1-A)^{2N}. \tag{9}$$

The number of layers in the sample is given by relation $N \simeq x/d$; x being thickness of the sample and d is the average diameter of particle. Eq. (9) is useful to calculate reflectance of semitransparent particulate sample from size and refractive index of particle.

3. Experimental

To study the performance of proposed relation, particulate samples of white, golden yellow and grey glass were prepared by rigorous grinding of respective plate glass. Particle size in each sample was controlled by passing the powdered samples through series of sieves of varying pore size attached to a mechanical vibrator. Six particulate samples as shown in Table 1 of varying particle sizes were selected for the study.

Table 1. Average particle size in particulate sample.

Name of sample	Abbreviation	Average size in micron
White glass-1	WG-1	87.20
White glass-2	WG-2	54.50
Grey glass-1	GG-1	106.50
Grey glass-2	GG-2	50.00
Grey glass-3	GG-3	40.00
Golden-Yellow glass	GYG	97.70

Average particle size in each sample was determined using projection microscope. The microscope is equipped with objectives having magnification 125X, 250X, 500X and 1000X. For each combination of objective and eyepiece the projection screen was calibrated. Particles were then uniformly spread on a microscope slide using appropriate technique. Particle size of large number of particles seen on a calibrated screen were measured and histogram for each sample was constructed. The average particle diameter was then determined using relation $d_i = \sum N_i d_i / N_i$. N_i being number of particles measured. Measurements were made on about 600 particles in each case. Average particle size in each powdered sample is given in Table 1.

To prepare semitransparent measurement sample (also called as layer at incomplete hiding in colour science) a sample holder plate with circular pit of dimension of 26 mm diameter and 2.5 mm depth was taken. Eastman Kodak Barium Sulphate powder added to this pit was then pressed and surfaced using a glass rod of 25 mm diameter with its ends polished to an accuracy of $\lambda/4$. This process was continued till a small fraction of pit remained unfilled. This hard white flat bed of $BaSO_4$ worked as a substrate for semitransparent particulate layer. Glass powder was gently spread over the substrate and surfaced with fine edge blade without applying any pressure. Number of particle layers in the sample were determined from thickness of layer and average size of particle.

The sample was then kept in horizontal position at the sample port of the integrating sphere of DATACOLOR spectrophotometer. It is an abridged spectrophotometer and records diffuse reflectance of the sample for wavelengths 400(20)700 nm. Reflectance spectra of all samples were recorded with measurement aperture, above the sample, maintained at 10 mm diameter.

The absorption indices k of all samples for wavelengths 400(20)700 nm were determined from reflectance measurements. For this purpose particulate samples were diluted with Eastman Kodak $BaSO_4$ whose absolute reflectance and scattering coefficients are known [15]. Reflectance of thick layer (also known as layer at complete hiding in colour science) of mixture is measured. Absorption indices at respective wavelengths were then determined using K–M theory equation and method proposed by Lindberg and Laud [16].

4. Results

The diffuse reflectance spectra recorded on a spectrophotometer for six particulate samples prepared from three types of glasses are shown in Figures 2 to 4 by a continuous line. White, and grey glass powders exhibit almost constant reflectance over entire visible spectral range. Absorption of radiation of grey glass powdered sample exhibit low reflectance at all the wavelengths in visible spectrum as compared to that of white glass powders. Golden yellow glass powder sample exhibit absorption peak in violet-blue region of the spectrum.

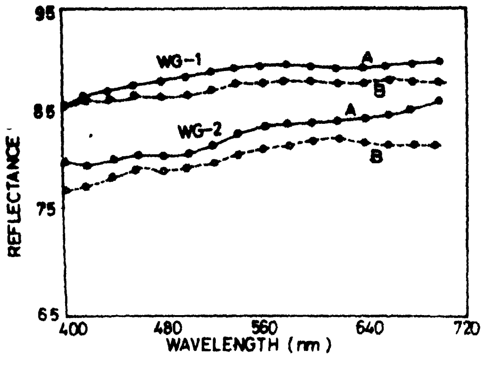

Figure 2. Comparison of experimentally measured (Curve A) and theoretical calculated (Curve B) reflectance spectra of semitransparent particulate samples of white glass.

The reflectance spectra of these particulate systems were also generated using theoretical eq. (9), proposed in this paper. Refractive index 'n' of glass do not vary significantly in visible spectral range. Therefore, $n = 1.5$ was taken for calculating reflectance spectra of all particulate samples. The absorption index k significantly varies with wavelengths of radiations even in visible spectral range. The values of k were therefore, determined for 16 wavelengths 400(20)700 nm using the method proposed by Lindberg and Laud [16]. Absolute values of R_g, the reflectance spectra of Eastman Kodak Barium Sulphate are taken from data published by

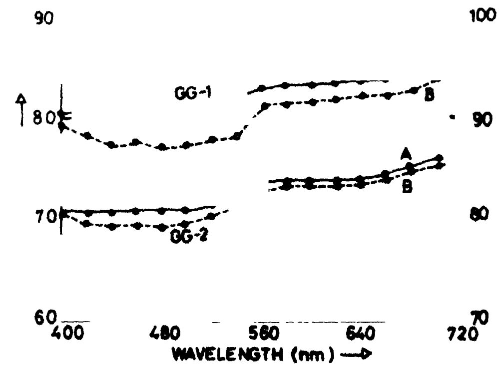

Figure 3. Comparison of experimentally measured (Curve A) and theoretical calculated (Curve B) reflectance spectra of semitransparent particulate samples of grey glass Ordinate scale on right hand side is for particulate system GG-2.

Patterson *et al* [15]. Values of n, k, d and R_g so obtained were used to construct diffuse reflectance spectra of powdered samples. Theoretically predicted diffuse reflectance spectra are shown by dotted lines in respective figures. Figures 2 to 4 show that the reflectance spectra calculated using proposed theoretical expression for semitransparent particulate samples agree reasonably well with measured spectra.

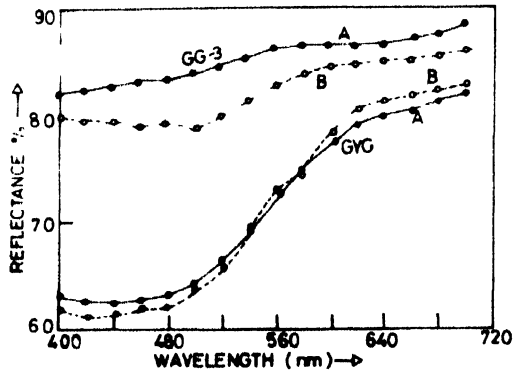

Figure 4. Comparison of experimentally measured (Curve A) and theoretical calculated (Curve B) reflectance spectra of semitransparent particulate samples of grey and golden yellow glass.

The work reported in this paper, is a part of outcome of project on colour science. Here, we have proposed a method to determine colourimetric curves (reflectance spectra) considering the discrete nature of the sample. In colour physics, the performance of theoretical formulation to generate the colourimetric curve is judged by calculating CIE (International Commission of Illumination) colour and colour difference parameters. According to CIE, the colour of the object is quantified from reflectance spectra in visible spectral range using relations,

$$X = \sum_{\lambda=400}^{700} R P \bar{x} \quad Y = \sum_{\lambda=400}^{700} R P \bar{y} \quad Z = \sum_{\lambda=400}^{700} R P \bar{z} \tag{10}$$

X, Y, Z are called as CIE tristimulus values of the colour. R is reflectance of the sample $P\bar{x}$, $P\bar{y}$ and $P\bar{z}$ takes care of the CIE illuminant and standard observer. Values of these parameters are available in standard data tables [17], for different illuminants. We have made calculation for CIE illuminant D_{65} which closely resemble to a day light source.

To calculate colour difference parameter CIELAB colour coordinates were calculated using relations [18],

$$L^* = 116(Y/Y_n)^{1/3} - 16,$$

$$a^* = 500\left[(X/X_n)^{1/3} - (Y/Y_n)^{1/3}\right],$$

$$b^* = 500\left[(Y/Y_n)^{1/3} - (Y/Y_n)^{1/3}\right], \tag{11}$$

X_n, Y_n, Z_n are tristimulus values of CIE Illuminant and are tabulated elsewhere [18]. The difference in CIELAB colour parameters calculated from predicted and measured spectra are calculated as DL^*, Da^*, Db^*. The colour difference parameter DE is then determined by relation

$$DE = \left[(DL^*)^2 + (Da^*)^2 + (Db^*)^2\right]^{1/2} \tag{12}$$

This colour difference parameter DE can be used as a measure of performance evaluation of theoretical formulation to predict the reflectance spectra and colour of the sample. In practice for light colours, $DE \leq 1.5$ considered as within the accepted tolerance limit. CIE colour and colour difference parameters calculated from reflectance spectra of respective samples are given in Table 2. The colour difference calculated from measured and calculated reflectance spectra are within the accepted tolerance limit for all particulate samples. For GG-3 sample the value of DE = 1.95 which is to some extent outside the accepted tolerance limit in colour science.

Table 2. CIE colour and colour difference parameters calculated from experimental and theoretical reflectance spectra of powdered samples.

Name of sample	Nature of data	Tristimulus values			Colour difference DE	No. layers in sample
		X	Y	Z		
WG-1	experimental	83.646	88.363	93.358	0.73	3
	theoretical	82.275	86.763	91.750		
WG-2	experimental	78.157	82.102	86.052	0.98	5
	theoretical	76.011	79.942	83.816		
GG-1	experimental	78.216	82.102	85.857	1.39	3
	theoretical	76.106	79.490	82.960		
GG-2	experimental	78.561	82.566	86.569	0.65	3
	theoretical	77.844	81.589	85.153		
GG-3	experimental	80.936	85.122	88.957	1.95	5
	theoretical	78.201	81.675	84.480		
GGY	experimental	69.581	72.111	67.535	1.210	2
	theoretical	69.708	71.233	66.235		

5. Summary and discussion

A theoretical expression correlating reflectance of semitransparent powdered samples with particle size and refractive index is derived. The performance of the proposed expression is studied by comparing measured reflectance spectra with theoretically calculated ones. The overall performance evaluation of the proposed expression is made by determining colour difference between the measured and calculated colourimetric curves. The colour difference so calculated agree within accepted tolerance limit. Therefore, for practical purposes the proposed expression can be used either to assess the reflectance spectra of semitransparent particulate layer from size and refractive index of particle or particle size in particulate sample from reflectance measurements.

The apparent source of error lies in the determination of number of layers N in each sample. Particles in powdered samples are not spherical in shape and therefore the random orientation of particles in the measurement sample may give inaccuracy in determination of N. Again polydispersity in particle sizes in all samples will also adversely affect the accuracy of final results. Further in particle model theory, the expression for parameter 'A', characterizing the absorption of particle, is in complicated form. For weakly absorbing particles this expression reduces to simple form as given in this paper. Therefore, the proposed theoretical expression is strictly applicable to weakly or non-absorbing particles. The particulate systems used in the present study satisfy this requirement.

Unfortunately, mathematical method employed for theoretical formulation appears as hybrid of technique used in continuum media and particle model theories. But this is not so. The interaction of radiation with particulate matter is expressed through only absorption characteristics of particles. Particles in the sample being large, the Rayleigh type scattering is assumed to be absent. Therefore, no scattering parameter is included in the theoretical derivation unlike in any continuum media theory. Further, the expression for parameter 'A' used in this paper is derived by Simmons using laws of geometrical optics. The work reported in this paper is therefore, a contribution to particle model theories.

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